REMARKS

The present application accompanies a Request for Continued Examination under 37 CFR 1.114. Applicants request that the present application be withdrawn from appeal, and that prosecution of the application be reopened before the Examiner. Claims 1-22 and 28 are presently cancelled. Claims 23-27 and 29-31 were previously cancelled. New claims 32-55 are presently added. Support for the new claims is found in the claims as filed and in the specification at, for example, 11:17-18 and 22, 12:10-14, 15:1-3 and 25-29, and the Examples section.

The present invention is directed to methods for producing colored diamonds, including neon yellow-green diamonds, yellowish green diamonds and greenish yellow diamonds, from natural brown diamonds.

The Arguments made in the Amendments dated October 9, 2003 and March 8, 2004 in response to the Office Actions are hereby incorporated by reference. Applicants respectfully submit the following arguments in support of patentability.

I. The Claims Are Not Obvious Under 35 U.S.C. §103(a) Over Strong Alone Or Taken With Wentorf.

Strong (U.S. 4,124,690) teaches the conversion of Type Ib or mixed Type Ib-Ia natural diamond having a starting color of "greenish-yellow" to "yellow", to at least a shade of lighter yellow, i.e. to a very pale yellow or a "colorless" diamond (Strong 6:40-50). In the method of Strong, Type Ib nitrogen is at least partially converted to Type Ia nitrogen.

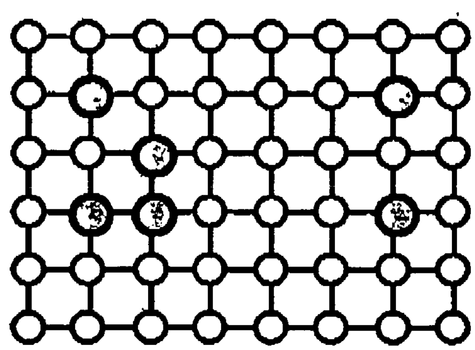
Wentorf (U.S. 3,609,818) discloses a high pressure, high temperature apparatus for the preparation of stronger, thicker diamond "compacts," wherein a mass of diamond crystals is infused with a molten catalyst material.

The presently claimed invention is directed to a method for changing the color of a brown natural diamond, wherein the brown natural diamond is Type IaB, Type IaA/B, Type IaA or Type Ib diamond. The method of claim 32 includes placing the diamond in a pressure transmitting medium, consolidating the pressure transmitting medium into a pill, exposing the pill to an elevated pressure of at least 10 kilobars and an elevated temperature of greater than

1500°C within the graphite stable or diamond stable range of the carbon phase diagram for a time sufficient to change the color of the diamond, and recovering the diamond having a color. The method of claim 47 includes placing the brown natural diamond in a pressure transmitting medium, subjecting the medium to a sufficiently high pressure and high temperature for a time sufficient to change the color of the diamond to a fancy color and recovering the diamond.

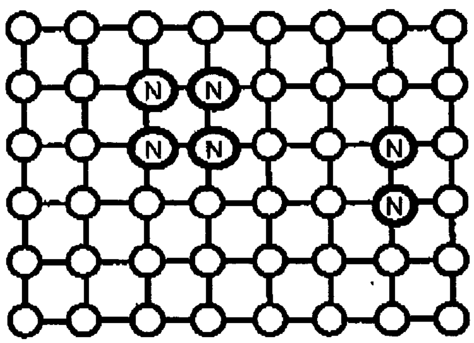
The claims are not obvious under 35 U.S.C. §103(a) over Strong, alone or taken in consideration with Wentorf. Strong fails to teach or suggest a method for changing the color of brown natural diamond, as claimed herein. Strong does not teach or suggest exposing a brown natural diamond to high pressure and high temperature for a time sufficient to change the diamond's color, and rather solves another problem which is that for converting a diamond with Type Ib nitrogen that is greenish yellow to yellow in color into a diamond with Type Ia nitrogen that is lighter yellow or colorless.

In Type Ib diamonds, most of the nitrogen is atomically dispersed. (Strong 1:17-18). Isolated nitrogen atoms are also known as C Centers, and where these are the primary color center, and in the absence of colorization from plastic deformation or strain, they give a diamond a yellow color. (See Application at 2:2 and 2:29-31). Type Ib diamond lattice has the general structure shown below (with open circles representing carbon atoms, grey circles representing single nitrogen atoms):



Strong converts diamonds having primarily Type Ib nitrogen into diamonds having Type Ia nitrogen, or mixed Type Ia and Ib nitrogen structures. In Type Ia diamonds, most of the nitrogen is aggregated (Strong 1:15-16). The aggregated nitrogen in Type Ia

diamonds appears as nitrogen pairs (called A Centers) or clusters of four nitrogen atoms (called B Centers). These color centers in Type Ia diamond lattice have the general structure shown below:

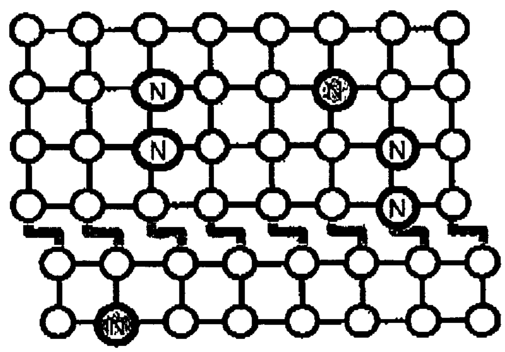


If all of the nitrogen is found in A or B Centers, the diamond will be colorless (See Application 2:28-29; Strong 6:40-46). A diamond with both A or B Centers and C Centers will have some residual yellow color caused by the presence of C Centers (See Application 2:29-3:1; Strong 2:50-56 and 6:40-50).

Strong teaches <u>reducing or eliminating</u> color from diamonds with Type Ib nitrogen by converting Type Ib nitrogen structure to Type Ia nitrogen structure. Strong does not teach any method of converting a colored diamond from one color to another; that is, Strong does not teach the creation of new color centers. Strong's process appears to cause single nitrogen atoms to aggregate into nitrogen pairs or clusters of four nitrogen atoms. Thus, Strong treats diamonds with C Centers in order to reduce the number of C Centers.

The present claims are directed to changing color or creating a new color center that <u>adds</u> color to brown natural diamonds, not to making diamonds colorless. In natural diamonds, brown is not merely a color, but is also a characteristic of diamond structure. Brown color in natural Type I diamonds can arise from the presence of mixed color centers as well as plastic deformation in the crystal (See Application at 4:3-13 and Alan T. Collins et al., *Colour Changes Produced in Natural Brown Diamonds by High-Pressure, High-Temperature Treatment*, Diamond and Related Materials 9, 113 (2000), specifically page 118 (attached hereto

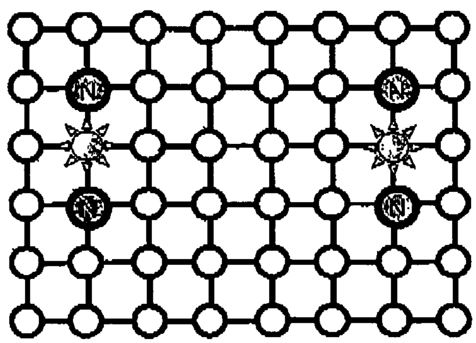
as *Appendix 1*). Brown natural diamonds may comprise A, B, C Centers, or strain induced color or combinations thereof. An example of such a plastic deformation and its treatment is illustrated in the Figure presented below.).



Strong describes treating a yellow diamond, i.e. one that appears to lack any structural characteristics of brown diamonds. Strong's diamond contained a large proportion of optically active C Centers and no strain; if significant strain had been present in the Strong diamond, it would have been brown. The present invention, however, treats diamonds that are brown prior to treatment. Accordingly, the starting diamond used by Strong is structurally different than that of the presently claimed invention.

The present invention causes a change in the color of brown diamonds by the creation of new color centers, such that the resulting diamond has a color. As described in the specification, this may be accomplished by the formation of H3 Centers by HPHT treatment (See Application at 11:15-12:14). An H3 Center is known to one skilled in the art as a nitrogen pair that surrounds a vacancy in the diamond lattice, as shown in the diagram below. HPHT annealing can lead to the formation of H3 centers by the combination of A centers with vacancies, imparting a color. Thus, claims 32 and 47 claim processing under conditions that change a brown diamond to a colored diamond of a different color, which is neither taught nor suggested by Strong or Wentorf. The method may increase the ratio of H3 Centers to A Centers in the annealed diamond, as claimed in dependent claims 40 and 51. The H3 Centers may impart a neon yellow-green, yellowish green or greenish yellow color to the diamond, as claimed in dependent claims 38 and 52. Thus, there is a particular structural change on the atomic level

associated with starting with a brown natural diamond and changing its color by a high pressure high temperature process to create new color centers. The recovered diamonds of the invention therefore include a changed structural arrangement, i.e. the creation of a new color center, which imparts a color to the diamond.



Strong does not teach or suggest a structural change in brown natural diamonds as a result of HPHT annealing, as claimed herein, and does not appreciate that such structural change can create new color centers in the diamond that impart new color.

Further, Strong teaches away from the claimed invention in its quest for a lighter and/or colorless diamond. The objective of Strong is to reduce or eliminate the color of Type 1b or mixed Type Ib-Ia diamond crystals, i.e. starting with "a greenish-yellow to a yellow" diamond (Strong 2:48) to yield Type Ia diamond with "*a very pale yellow and/or a colorless crystal*" (Strong 6:47-48, emphasis added). The present claims, by contrast, recite a method that is aimed at changing (rather than reducing or eliminating) the color of a brown natural diamond.

In summary, Strong fails to disclose a starting brown natural diamond, fails to teach or suggest applying Applicant's claimed high pressure high temperature process to a brownish natural diamond to impart color, and fails to teach or suggest a change in diamond color associated with the formation of a new color center. For all of the above reasons, Applicants respectfully submit that the claims are patentable over Strong.

Furthermore, Wentorf fails to cure the deficiencies of Strong. In particular, Wentorf fails to teach or suggest changing the color of a diamond at all, let alone changing the color of a brownish natural diamond. Moreover, Wentorf does not teach the use of a pill as recited in claim 32.

One skilled in the art would not be motivated to combine the teachings of the Strong reference with those of Wentorf. First, the method of Wentorf relates to the formation of "compacts" which are polycrystalline diamond masses (Wentorf 1:31-32 and 12-13) for use in abrading tools (Wentorf 2:1-2). It does not relate to the problem of HPHT annealing of diamonds to impart a color change. In particular, Wentorf fails to teach or suggest a method of converting Type Ib nitrogen to Type Ia nitrogen diamonds, or even any diamonds, and therefore one skilled in the art would not look to Wentorf to supplement the teachings of Strong to obtain the presently claimed invention. Applicants respectfully submit, therefore, that Wentorf is nonanalogous art, and as such should not be applied against the presently claimed invention.

Second, Wentorf actually teaches away from the use of a pill as recited in claim 32. One characteristic of the claimed pill is that it must transmit hydrostatic pressure without loss as a continuum onto diamond surfaces in the HPHT apparatus (See Application at 15:8-9). Wentorf, however, appears to address the opposite goal, that of creating a "mechanically unstable" assembly enclosing a treated mass (Wentorf 4:23 and 54). Wentorf describes cylinder 19 enclosing a mass of diamond particles and graphite (Wentorf 3:49-50). Wentorf teaches that compaction occurs within the enclosed mass, when subjected to pressure and temperature, which causes cracking of the mass (Wentorf 4:48-54). The cracking of the mass enables the movement of metal catalyst and pressure distribution material into the cracks (Wentorf 4:62-64). One of skill in the art would not be motivated by the teaching of Wentorf to use a pill as in claim 32 because Wentorf does not transmit hydrostatic pressure without loss as a continuum onto the treated mass. Moreover, cracking within the annealed mass as noted by Wentorf would be an undesirable result in the presently claimed invention.

For the foregoing reasons, the claims are not rendered obvious by Strong alone or in combination with Wentorf. Claims 33-45 and 47-55 depend directly and indirectly from

independent claims 32 and 46 and further define the method of the present invention. These claims further distinguish the claimed invention from the disclosures of Strong and Wentorf.

II. The Claims Are Not Obvious Under 35 U.S.C. 103(A) Over Cannon

Cannon (U.S. 3,134,739) discloses a method of whitening diamonds and changing the electrical characteristics of diamonds. Cannon relates to an electrically conductive diamond containing aluminum atoms introduced through a diffusion process. In particular, the method of Cannon as recited at 6:66-70 is directed to the production of "colorless diamonds".

As described above with regard to Strong, the presently claimed invention is directed to changing or imparting new color to brown natural diamonds, not to making diamonds colorless. Cannon appears to teach a method that yields colorless diamonds, which is distinct from the presently claimed invention.

Appellants further submit that the teachings of Cannon that the Examiner is relying upon, and Cannon itself, is inoperable. Attached is an affidavit (Appendix 2) executed by Dr. Suresh Vagarali. This affidavit was previously submitted to the Examiner on October 9, 2003. In the affidavit, Dr. Vagarali establishes that upon repeating the Examples in Cannon, the results as described in Cannon are not achieved. In other words, a brown diamond will not change color when treated in accordance with the methods taught in Cannon. As stated in this declaration, Dr. Vagarali conducted four experiments to evaluate the effect of pressure and temperature for changing the color of diamonds as disclosed in Cannon. The experiments were run to determine the veracity of the Cannon invention as defined by the statement, "At high pressures and temperatures, diamonds grown become more clear and white, but aluminum diffusion provides a more marked and contrasting change to colors." (Cannon, col. 6 line 73 to col. 7, line 1). From the results of the experiments as shown in the affidavit, it is clear that the method disclosed in Cannon does not teach or suggest a method for changing the color of a diamond, let alone changing a brown natural diamond to a diamond having color as recited in Appellants' claimed invention. Cannon does not disclose any combination of conditions that will change the color of a brown natural diamond, and does not teach a time sufficient to change the color of a diamond. Moreover, Claim 47 claims pressures and temperatures that will impart a

fancy color in the diamond. The experiment described in the attached declaration shows that Cannon does not teach such a result.

Furthermore, the present claim 32 recites that the temperature is greater than 1500° C. Cannon does not teach temperatures greater than 1500° C, and there is nothing in Cannon to motivate one of skill in the art to increase the temperature to this range.

CONCLUSION

In summary, the claims of the present invention define a process for changing the color of a brown natural diamond that is a Type IaB, Type IaAB, Type IaA or Type Ib diamond. Applicants respectfully submit that the claims are in condition for allowance, and request early notification of allowance.

A Request for Continued Examination (RCE) Transmittal including an authorization to charge the required RCE fee of $790.00 to Deposit Account No. 50-0436 accompanies this submission. The Commissioner for Patents is hereby authorized to charge any additional fees which may be required to Deposit Account No. 50-0436. Please refund any overpayment to Deposit Account No. 50-0436.

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DIAMOND AND RELATED MATERIALS

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Colour changes produced in natural brown diamonds by high-pressure, high-temperature treatment

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Abstract

Absorption and luminescence spectra have been measured for natural brown diamonds before and after high-pressure, high-temperature (HPHT) treatment at 1700–1800°C, and after HPHT treatment at 2025°C. The reduction of the brown colour noted in diamonds with low nitrogen concentration is attributed to the annealing of plastic deformation. In nitrogen-containing diamonds the vacancies released during this annealing are trapped to form N–V–N centres. In addition, the photoluminescence band with a zero-phonon line (ZPL) at 2.526 eV (490.7 nm), characteristic of decorated slip traces, is reduced in intensity during this process, confirming that changes are taking place at the slip traces which have resulted from the plastic deformation. At the lower annealing temperatures the N–V–N centres are in the neutral charge state, giving rise to the H3 absorption band, with a ZPL at 2.463 eV (503.2 nm) and resulting in a yellow colour. At the higher annealing temperature some nitrogen aggregates decompose, producing single substitutional nitrogen which is an electrical donor. Consequently some N–V–N centres are in the negative charge state, and give rise to the H2 absorption band with a ZPL at 1.257 eV (986.9 nm). The combination of absorption in the H2 and H3 bands gives the diamonds a yellow-green or green colour. Annealing at the highest temperature, at pressures very close to the diamond/graphite transition, seems to be effective at reducing the non-radiative recombination channels in the diamonds, and, in white light, many specimens exhibit bright green luminescence, produced by absorbed energy being re-emitted in the H3 band. To the eye these processed diamonds appear similar to the very rare, naturally-occurring, 'green transmitters'. However, because the latter have resulted from much lower geological temperatures, acting over much longer periods of time, they contain negligible concentrations of single substitutional nitrogen and consequently have low H2 absorption.

Keywords: Colour enhancement; HPHT processing; Natural diamonds; Optical spectroscopy

1. Introduction

In this paper we report measurements carried out to understand the processes occurring when the colour of natural diamonds (particularly natural brown diamonds) is changed by annealing at high pressure and high temperature (HPHT). We present the first evidence that, in the temperature régime where the colour changes take place, annealing phenomena are occurring at slip traces.

The majority of natural diamonds have a brown colour [1] which makes them less attractive as gemstones. However, recent research has shown that, when natural brown type IIa diamonds are annealed at HPHT, the intensity of the brown colour is substan-

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tially reduced [2–4]. (Type IIa diamonds are those specimens, which contain too little nitrogen to be detected using infrared absorption spectroscopy.)

Following this disclosure, very recent studies have been reported [5] on the HPHT annealing of natural brown diamonds which had not been pre-selected to choose exclusively type IIa specimens. In this case the majority of the specimens changed from brown to yellow or yellow/green, and many of the stones exhibited an intense green photoluminescence when excited with blue or ultraviolet light.

In the present investigation we have measured the absorption and luminescence spectra, in the ultraviolet, visible and near-infrared spectral regions, of a number of natural brown diamonds before and after they have been annealed in a high-pressure press. We have also examined the absorption spectra in the visible and near-infrared regions of three diamonds after they had been processed commercially at higher temperatures than those used in our own annealing measurements. In addition, absorption in the defect-induced one-phonon region (approx. 1350–400 cm^{-1}) of all the diamonds was measured to estimate the concentrations of nitrogen present.

These measurements, when considered in the light of many previous studies of diamond, allow us to propose a model for the processes occurring. The measurements also show that, in many cases, the spectra of the processed diamonds are unlike those which are found in nature.

2. Experimental

2.1. Selected brown diamonds

Fourteen pieces of natural diamond with brown colour, weighing 10–50 mg (0.05–0.25 carat), were selected from cut (i.e. faceted) or rough crystals. Five rough crystals were polished to exhibit parallel (110) surfaces, which enabled us to observe the distribution of nitrogen impurities by infrared spectroscopy.

The diamonds were heated at 6 GPa and 1700–1800°C for 5 h using a belt type high pressure apparatus [6]. Each crystal was embedded in powdered NaCl, boron nitride or graphite. Although one crystal was broken into two pieces when recovered from the high pressure cell, the others did not have serious damage. The surfaces of the crystals became frosty, either because of growth (when packed in graphite) or dissolution, and the cut diamonds were re-polished to observe any colour change.

Photoluminescence spectra were taken for all of the crystals at −160°C, using a Renishaw Raman Imaging Microscope fitted with a Kimmon He–Cd laser (325 nm) and a Linkam cooling stage. This equipment is designed for microscopic measurements, and we took spectra at 6–10 points for each sample.

Absorption spectra from 400 to 800 nm were recorded for three crystals at liquid nitrogen temperature before and after the treatment.

Nitrogen concentrations were measured with a Bomem M110 FTIR spectrometer fitted with a Spectra Tech IR-PLAN microscope. From three to 10 different regions were measured for each crystal, using a 200-μm square aperture. Infrared spectra were not taken for the crystals after heat treatment, because no change was expected at the heating temperature used.

2.2. Commercially processed diamonds

Two yellow/green brilliant-cut diamonds (0.63 and 0.33 carat) and one rough green diamond (0.75 carat) that had been processed by NovaDiamond, Inc. were also examined. These diamonds were originally low-quality brown specimens, and had been heated to approximately 2025°C at a pressure of 6 GPa for approximately 30 min [5].

The absorption spectra of these diamonds were measured from 400 to 1000 nm at liquid nitrogen temperature, and the infrared absorption spectra in the defect-induced one-phonon region were measured with a Nicolet Avatar FTIR instrument fitted with a beam condenser.

3. Results

3.1. Selected brown diamonds

We begin by reporting the results on diamonds examined before and after HPHT treatment, then, in Section 3.2, we consider data obtained from the commercially processed specimens. The optical centres described (A nitrogen, B nitrogen, H3, N3, 1.945-eV and 491-nm centres) will be discussed in more detail in Section 4.

3.1.1. Visual inspection

The colours of the faceted diamonds were compared by eye against master stones before and after treatment. In all cases the intensity of the brown coloration was reduced.

The three diamonds which were examined using absorption spectroscopy in the visible spectral region (Section 3.1.4) were also examined under an optical microscope before and after treatment. It was clear from the surface texture on these diamonds that they had experienced severe plastic deformation. The brown colour observed before treatment was not uniform, but was striated with the striations oriented in the direction of slip. This effect is well-known with natural brown

Fig. 1. The 'tatami' pattern characteristic of plastic strain in a brown diamond, obtained by photographing the diamond with transmitted light when placed between crossed polarisers.

diamonds, and the striations are often referred to as 'coloured graining' in the gem trade [1]. Following the HPHT treatment these striations were less visible, and their colour had changed from brown to yellow.

Observation of the crystals using transmitted polarised light revealed fine textures as shown in Fig. 1. The texture is similar to the so-called 'tatami' structure [7]. The presence of this pattern confirms the visual observation that the crystals had suffered plastic deformation.

The changes in absorption of these diamonds were assessed spectroscopically (Section 3.1.4), but examination under the microscope before and after treatment gave the impression that for one diamond (K3) the colour was less intense, and had changed from brown to pale yellow-brown; the other two diamonds (E3 and L1) had yellow components to the colour which were not evident before treatment.

3.1.2. Infrared absorption measurements

Absorption measurements in the one-phonon defect-induced absorption region showed that most of the diamonds contained nitrogen as mixtures of A and B aggregates. The B/A ratios were variable from 20% to almost 100%. The highest concentration of nitrogen was estimated to be 500 ppm, while one diamond (K3) was a near-type IIa with very little nitrogen. Measurements at different locations showed that the nitrogen distribution was inhomogeneous in many of the specimens.

3.1.3. Photoluminescence measurements

Fig. 2 shows a typical example of photoluminescence spectra observed in this study before and after heat treatment. The feature labelled D is the Raman line produced by the 325-nm laser and can be used to assess the relative strengths of the other features in the spectrum. Prominent among these are the zero-phonon lines at A (491 nm), B (503 nm, H3) and C (415 nm; N3).

We see that after the HPHT treatment the 491-nm line has been reduced to approximately one-fifth of its initial intensity, the N3 system has increased by approximately a factor of 4 and a substantial H3 band has been produced where very little was observed initially. The broad band with a maximum near 740 nm has also decreased in intensity following the annealing.

Of 14 diamonds investigated, nine exhibited the photoluminescence peak at 491 nm. Following heat treatment the peak either annealed out completely or decreased considerably, as illustrated in Fig. 2. On the other hand, the luminescence intensities of the H3 and N3 bands generally increased.

3.1.4. Absorption measurements in the visible region

Fig. 3a shows the absorption spectrum of diamond L1 before heat treatment. This spectrum is typical of that for nitrogen-containing brown diamonds. The absorption progressively increases from low energy to high energy; superimposed on this continuum absorption is a broad peak at approximately 2.2 eV, a weak H3 absorption band and a very weak N3 band (the zero-phonon line is just visible).

Fig. 3b shows the spectrum after annealing. The 2.2-eV band is still present, but the continuum absorption has been reduced in intensity. There is a small increase in the N3 absorption and a huge increase in the H3 absorption. The result of these variations is to change the original brown colour to a pronounced yellow colour.

Similar results were obtained with diamond E3. Originally this specimen had some continuum absorption and appreciable N3 absorption, giving the stone a yellow-brown colour. There was no detectable H3 absorption, but there was a weak band with a zero-phonon

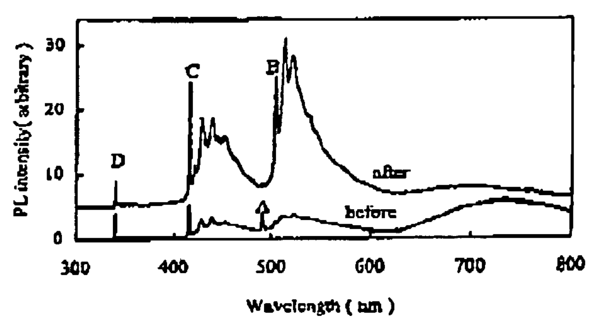

Fig. 2. Photoluminescence spectrum of a brown diamond, measured with the sample at −160°C, before and after annealing at 1800°C. The features labelled A–D are respectively the 491-nm, H3 and N3 zero-phonon lines and the Raman line excited by the 325-nm laser. The spectra have been displaced vertically for clarity.

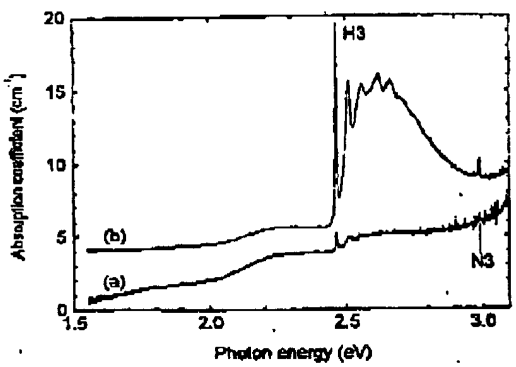

Fig. 3. Absorption spectra of a brown diamond, measured with the sample at 77 K, (a) before, and (b) after annealing at 1600°C. The spectra have been displaced vertically for clarity.

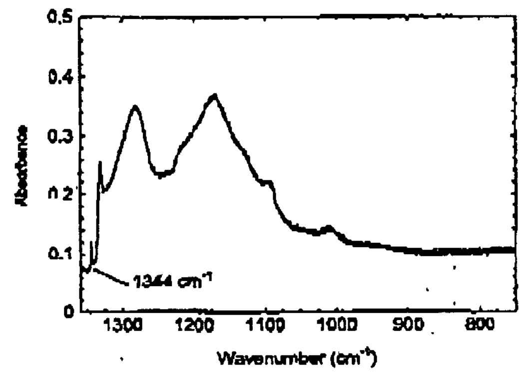

Fig. 4. Infrared absorption spectrum in the defect-induced one-phonon region of a faceted specimen after HPHT processing at approximately 2025°C. The diamond was at room temperature and the spectral resolution was 0.5 cm^{-1}.

line at 2.386 eV. After annealing, the N3 absorption increased by approximately a factor of two, an appreciable H3 band was produced and the 2.386-eV system annealed out. Again, this resulted in the colour becoming less brown and more yellow after the heat treatment.

Diamond K3 which had a low nitrogen concentration showed just a featureless continuum before annealing. After annealing, the intensity of the continuum absorption decreased by approximately a factor of 2 and weak absorption was produced in the 2.2-eV, H3 and N3 bands. This diamond, originally brown, was a pale yellow-brown after treatment.

Following the measurements described in Section 3.2, the measurement of the absorption spectrum of diamond L1 was extended to cover the range 800–1000 nm (1.55–1.24 eV), but no additional features were found.

3.2. Commercially processed diamonds

The two faceted specimens that had been processed from natural diamonds that were originally brown, had a yellow-green colour, and the larger stone (0.63 carats) still had a brown component to its colour (this was evident when the two diamonds were examined side-by-side). In tungsten light on the microscope stage the two diamonds exhibited bright green luminescence. Diamonds with these characteristics are known in the gem trade as 'green transmitters' [1] and are very rare in nature. The description 'green transmitter' is rather misleading [1]. The light transmitted by these diamonds is predominantly yellow, but the diamonds appear green in white light because of their intense luminescence. The H3 optical centre is responsible for this behaviour; the blue and violet components of white light are absorbed and the emission is in the green spectral region.

The third (rough) diamond investigated, also originally brown, had a distinct green colour (i.e. the light *transmitted* was green), and, in addition, exhibited some green luminescence.

3.2.1. Infrared absorption measurements

Infrared absorption spectra were measured for all three diamonds in the defect-induced one-phonon region. The spectrum for the large faceted diamond is shown in Fig. 4, and an approximate analysis shows that it contains approximately 70 ppm of nitrogen with more than 80% in the B form. The small faceted diamond contained approximately 300 ppm of nitrogen, with approximately 95% in the B form while the rough green diamond contained approximately 70 ppm nitrogen, mostly in the A form. Fig. 4 shows a well-defined sharp absorption peak at 1344 cm^{-1}, and this feature was also observed in the rough green diamond. It was not, however, detected in the smaller faceted diamond.

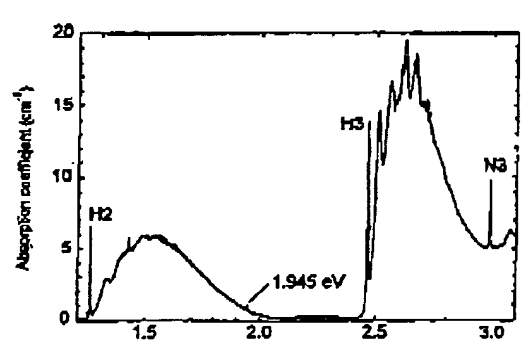

Fig. 5. Absorption spectrum in the visible and near-infrared regions of a rough diamond which had a green colour after HPHT processing at approximately 2025°C. The spectrum was measured with the diamond at 77 K.

The significance of this feature will be discussed in Section 4.

3.2.2. *Visible and near-infrared absorption measurements*

Fig. 5 shows the absorption spectrum of the green diamond in the spectral range 1.2–3.1 eV (1000–400 nm). The H2, 1.945-eV, H3 and N3 zero-phonon lines have been identified. The intense H3 band makes the diamond almost opaque at the blue end of the spectrum, and the strong H2 band causes appreciable absorption at the red end of the spectrum. The net result is a transmission window centred on approximately 2.25 eV (550 nm) in the green part of the visible spectrum.

A precise comparison of the absorption strengths in this rough diamond with those in the faceted diamonds is not possible because of the difficulty in determining accurately the optical path lengths. However, we can make the following semiquantitative observations.

In the large faceted diamond the H3 absorption was approximately half the strength of that shown in Fig. 5, and the H2 absorption was approximately quarter the strength. A well-defined 1.945-eV zero-phonon line was also present, at approximately three times the strength shown in Fig. 5. There was also a continuous absorption increasing from low to high energies, presumably a remnant of the original brown coloration.

The intensity of the H3 absorption in the smaller faceted diamond was comparable in strength with that for the larger faceted stone, but the H2 band was 5–6 times weaker, and there was no detectable absorption in the 1.945-eV zero-phonon line. Any remaining brown component was very small.

Because the H2 absorption is relatively weak in these two faceted diamonds the green component in their colour is much less than in the rough stone for which the spectrum is shown in Fig. 5.

4. Discussion

To understand the phenomena reported above we draw on a large background of previous work on natural and synthetic diamond. The presence of nitrogen is fundamental in controlling the colour of diamonds. Its properties have been reviewed previously [8] and the relevant aspects will be summarised here.

4.1. *Background*

Nitrogen is normally the major impurity in natural diamonds and HPHT synthetic diamonds. A very small fraction of natural diamonds has too little nitrogen to detect by infrared absorption spectroscopy, and such diamonds are known as type IIa. In most HPHT synthetic diamond, grown for short periods (typically a few minutes to several tens of hours, depending on the final size of crystal required) at relatively low temperatures (typically 1400°C), the nitrogen is present at a concentration of approximately 200 ppm, mostly on isolated substitutional lattice sites. At higher temperatures (1700–2100°C) the nitrogen becomes mobile and forms A aggregates (nearest neighbour substitutional pairs). Under more extreme annealing conditions (approx. 2400°C) some of the nitrogen forms B aggregates which comprise four nitrogen atoms symmetrically surrounding a vacancy. The majority of natural diamonds contain nitrogen in the A and B forms, and the activation energies for the aggregation processes, derived from laboratory experiments, are consistent with the diamonds having spent substantial periods (approx. 10^9 years) below the earth's surface at more modest temperatures (up to approx. 1200°C). Diamonds in which the nitrogen has aggregated are classified as type Ia.

The isolated substitutional nitrogen behaves as a deep donor, with an ionisation energy of approximately 1.7 eV; specimens in which this is the major impurity are called type Ib diamonds. The A aggregate, which is the major impurity in type IaA diamonds, also appears to have donor-like properties, with an ionisation energy of approximately 4 eV. No evidence has been obtained to show that the B aggregate is electrically active. Diamonds in which the B form of nitrogen is the dominant impurity are classified as type IaB.

Each of these three forms of nitrogen gives rise to a unique absorption band in the defect-induced one-phonon region of diamond, most of which lies in the range 400–1350 cm^{-1}. The majority of natural diamonds contain a mixture of A and B nitrogen, and by decomposing the absorption spectrum the concentration of each form of nitrogen may be determined. Some natural diamonds described as type Ib contain a mixture of single nitrogen and A aggregates, and again the concentrations of each form of nitrogen can be determined by decomposing the spectrum into two components. A very sensitive indicator that a diamond contains some single nitrogen is the presence of a sharp localised vibrational mode at 1344 cm^{-1}.

Absorption associated with transitions from the isolated substitutional nitrogen donor to the conduction band begin at approximately 2 eV in the visible region, and there is a slowly increasing absorption at higher energies. This absorption at the blue end of the visible spectrum gives the diamonds a yellow colour. Transitions from the A aggregate to the conduction band, and optical transitions that occur at the centre, give rise to absorption in the ultraviolet region. A high-quality diamond containing only A-nitrogen is therefore completely colourless.

When the B aggregate of nitrogen forms there is another minor product produced which, in optical studies of diamond, is referred to as the N3 centre. This has three nitrogen atoms on a (111) plane 'bonded' to a

common vacancy. Optical transitions at this centre give rise to the N3 absorption band, which has a zero-phonon line at 2.985 eV (415.2 nm) and a structured band to higher energy. There is another transition at the N3 centre which produces the broad N2 peak at 2.59 eV (478 nm) with weaker peaks at higher energy. In 'regular' diamonds (which make up the majority of diamonds containing B-nitrogen) the intensity of the N2 and N3 absorption is proportional to the concentration of the B form of nitrogen. This absorption gives the diamonds a pale straw-yellow colour and, in the gem trade, these specimens are known as cape stones.

Much of the above understanding of nitrogen in diamond comes from HPHT aggregation measurements [9–12]. The aggregation of single nitrogen to A aggregates may be represented by the equation

$$N + N \rightleftharpoons A \tag{1}$$

At the temperatures experienced by natural diamonds the reverse reaction is negligible, and the aggregation process goes virtually to completion over a very long period of time [11]. In the laboratory, at the temperatures necessary to achieve aggregation in a relatively short time, the reverse reaction is appreciable, and it is not possible to obtain complete aggregation. More importantly, in the context of the present paper, if a natural diamond containing only A aggregates is heated at approximately 2000°C, some of the aggregates decompose to form single nitrogen [10]. The diamond, previously colourless, then has a pale yellow colour.

As stated previously, among mined diamonds, brown is the most common colour [1]. In many cases this colour appears to be associated with plastic deformation, and the diamonds exhibit coloured graining running parallel to the slip lines in the specimen. The origin of this brown colour is not known. In diamonds containing B nitrogen a cathodoluminescence emission band with a ZPL at 2.526 eV (490.7 nm) can often be detected from the slip traces [13]. Furthermore, Brooks et al. [14] have produced this luminescence in a type IaB diamond using an indentation technique, confirming that the centre responsible for the emission is associated with plastic deformation.

Cathodoluminescence measurements enable individual slip traces to be examined, and it is seen that the emission is polarised with the E-vector lying along the slip line [13]. This emission band may also be observed as photoluminescence, and is frequently seen in brown diamonds, as we have noted in Section 3.1.3. Because the emission is not seen at all slip traces, it must be assumed that a slip trace producing this luminescence is 'decorated' with a defect centre. One possibility might be a B aggregate which has been sheared by the deformation, but this can only be speculation at the present time.

4.2. Radiation damage

Radiation damage in diamond using, for example, 2-MeV electrons, produces vacancies which are stable at room temperature. On annealing at approximately 800°C the vacancies become mobile, and, in a diamond containing nitrogen, become trapped at the various forms of nitrogen to produce new colour centres. In type Ib diamond a vacancy trapped at single nitrogen produces a $(N\text{–}V)^-$ centre with a ZPL at 1.945 eV and a vibronic absorption band to higher energy [15]. In type Ia diamond a vacancy trapped at the A or B form of nitrogen produces respectively an H3 or H4 centre [16]; these have vibronic absorption bands with ZPLs at 2.463 (H3) and 2.499 eV (H4). Absorption in the 1.945 eV band gives a diamond a pink or red colour, while absorption in the H3 or H4 bands results in a yellow, orange or brown colour. (The final colour in each case will depend on the colour of the diamond before irradiation, and the intensity of the absorption induced by the radiation damage and annealing.)

Absorption of light in each of the above absorption bands can result in luminescence to the low-energy side of the corresponding ZPL. In addition, the N3 centre, mentioned in Section 3.1.3, may also produce blue luminescence when excited in the ultraviolet spectral region. The quantum efficiency for the production of luminescence is very different in different diamonds. High concentrations of nitrogen in the A form severely quench the H3 and N3 luminescence [17]; this is probably a general phenomenon for luminescence centres in diamond. Other non-radiative decay channels also reduce the intensity of the luminescence produced.

When natural diamond containing a mixture of A and B nitrogen has been subjected to irradiation damage and annealing, as described above, H3 and H4 centres are formed. For a range of diamonds, Davies [16] showed that the ratio [H3]/[H4] is proportional to the ratio [A]/[B], where the brackets indicate the concentrations of defects, obtained by absorption spectroscopy. Some natural diamonds are found in which the H3 absorption occurs naturally. Natural brown diamonds, for which a typical absorption spectrum is shown in Fig. 3a, often have some H3 absorption, and occasionally yellow diamonds exhibit H3 absorption, sometimes in association with green luminescence (the so called 'green transmitters' mentioned previously in Section 3.2). Although these naturally coloured diamonds may contain nitrogen in both the A and B forms, the H4 absorption is usually undetectably weak.

Collins [18] examined the effect of 'high-temperature' annealing on diamonds that had been irradiated and annealed to produce the H3 and H4 absorption. In

particular, it was found that, when a diamond, which contained predominantly H4 absorption after annealing at 800°C, was further annealed at 1500°C, the H4 absorption was considerably reduced in intensity and the H3 absorption had increased, producing a situation more nearly like that seen in natural diamonds. Collins interpreted this behaviour as the H4 centre breaking up to form H3 centres and small concentrations of other defects like $(N-V)^-$ centres. In the context of the present paper those measurements show that the H3 centre is more stable than the H4 centre at the high annealing temperatures employed.

Collins [19] showed further that when synthetic diamonds that had been irradiated and annealed at 800°C were annealed again at 1500°C, substantial aggregation of the single nitrogen occurred, even though the temperature used was well below that required to produce aggregation in unirradiated specimens. He attributed this behaviour to a vacancy-enhanced aggregation phenomenon. During the annealing, some H3 absorption was produced as a result of vacancies being trapped at the newly-formed A centres.

Mita et al. [20] also investigated the effect of high-temperature annealing of synthetic diamonds that had previously been subjected to radiation damage and annealing at 800°C. Initially the diamonds had an intense pink colour because of absorption in the $(N-V)^-$ band. After annealing at 1700°C, a large fraction of the single nitrogen had formed A aggregates, the absorption due to the $(N-V)^-$ centre had become very weak, and the diamonds had an intense green colour as a result of absorption being produced in the H3 and H2 optical bands. (The absorption spectra were similar to those shown in Fig. 5.) Mita et al. also observed photochromic effects in which the intensity of the H3 absorption could be increased, and that of H2 decreased, and vice-versa, by irradiating the diamond with light of the appropriate wavelengths. These observations led them to propose that the H2 centre was a negative charge state of the H3 centre, and was favoured in their diamonds because the Fermi level was shifted well towards the conduction band, due to the presence of single substitutional nitrogen. Lawson et al. [21] subsequently carried out uniaxial stress measurements on the H2 and H3 zero-phonon lines and showed that the symmetries of the centres were the same and the shift rates of the ZPLs with applied stress were very similar, giving substantial support to the proposal by Mita et al.

The 'Fermi level' in diamond has to be interpreted rather differently from that used in silicon, for example. Even when diamond contains single substitutional nitrogen donors, it is still an insulator, and charge equilibrium throughout the crystal is not achieved. If we assume that the Fermi level is 'pinned' at the defect centre, then in the immediate vicinity of a single substitutional nitrogen atom the Fermi level will be approximately 1.7 eV below the conduction band, whereas in the immediate vicinity of an A aggregate the Fermi level will be approximately 4 eV below the bottom of the conduction band. Consequently defect centres can be observed in more than one charge state in the same diamond.

Finally in this section we note that, if a type Ia diamond that has been irradiated and annealed to produce H3 and H4 centres is subsequently given a prolonged annealing at 1400°C, some H2 absorption may be produced [22]. Woods and Collins [23] referred to a 'drab, unappealing green colour' being produced as a result of this process, but in some cases the green colour can be attractive [22].

4.3. Interpretation of HPHT annealing

The observations reported in this paper, taken with the information from Sections 4.1 and 4.2, allow us to propose the following model for the colour changes produced by the HPHT annealing of natural diamonds.

We have seen that, in many cases, the brown colour of the diamonds under investigation is associated with plastic deformation. In the vicinity of the lattice planes which have encountered slip there is likely to be a high concentration of broken bonds. We have also seen that, in diamonds containing nitrogen in the B form, there is a defect centre localised at the slip planes which gives rise to a luminescence band with a ZPL at 490.7 nm (2.526 eV). In some diamonds this defect can be present in sufficient concentrations to be observed using absorption spectroscopy [24].

When such diamonds are taken to temperatures and pressures where it is known that synthetic diamond can be grown, we propose that there will be some healing of any ruptured bonds at the slip planes. Such a process would result in the release of significant concentrations of vacancies and interstitials. Vacancies may also be released by the interaction between moving dislocations.

We consider first the annealing measurements carried out at 1800°C. Evidence that changes are occurring at the slip planes is the reduction in the intensity of the 490.7 nm luminescence, shown in Fig. 2.

In diamonds with negligible concentrations of nitrogen we may assume that the vacancies disappear by annihilation with the interstitials. Consequently no new colour centres are formed and the end result is a diamond in which the brown colour is greatly reduced. This phenomenon has been reported previously [2–4], and has been reproduced in the present investigation to a limited extent.

If the diamonds contain aggregated nitrogen, the vacancies are trapped by the nitrogen to form H3 centres (we have noted above that H4 centres are less

stable than H3 centres at high temperature, and so presumably do not form at all under these conditions). After the high-temperature annealing we therefore observe an increase in the H3 absorption (Fig. 3b). There is some nitrogen mobility at the temperature used, and it is perhaps not surprising that the absorption intensity of the N3 band also increases (Fig. 3b) although the processes involved here are less clear at the present time.

At the higher temperatures used commercially the reverse reaction in Eq. (1) becomes significant, and appreciable concentrations of single substitutional nitrogen are produced by the break-up of some A aggregates. This results in the localised shifting of the Fermi level towards the conduction band. Consequently, as well as the processes that occur for lower annealing temperatures (1800°C), some N–V–N centres will therefore be in the negative charge state and give rise to an H2 absorption band. In addition, because vacancies trapped at the single substitutional nitrogen form $(N–V)^-$ centres, absorption at the 1.945-eV ZPL may be detected, as in Fig. 5. In some cases it is also possible to observe, just outside the one-phonon defect-induced absorption, the 1344 cm^{-1} localised vibrational mode, characteristic of isolated substitutional nitrogen (Fig. 4). Two of the three commercially processed diamonds investigated showed the 1.945-eV ZPL and the 1344 cm^{-1} localised vibrational mode, and all had appreciable H2 absorption although, in only one diamond (Fig. 5), was this sufficiently intense to produce a green body colour.

It has been reported that, in order to obtain strong H3 luminescence, it is necessary to anneal the diamonds at 2025°C, and that, if slightly higher temperatures are used, the diamond graphitises [5]. More work needs to be carried out to understand why annealing at conditions close to the diamond–graphite transition increases the luminescence efficiency in some diamonds.

5. Summary

From the results of measurements that we have carried out before and after subjecting natural brown diamonds to annealing at 1800°C, and from studies made on similar diamonds that have been annealed to 2025°C, we have proposed a model for the processes involved.

At the lower temperature, partial healing of the plastic deformation associated with the brown colour releases vacancies and interstitials. In a type IIa diamond there is a mutual annihilation of these vacancies and interstitials, and the end result is simply a lightening of the brown colour. In a type Ia diamond, vacancies are trapped by the nitrogen to increase the concentrations of H3 and N3 centres. In this case the original brown colour is reduced, and the H3 absorption results in a yellow colour. The disappearance of the luminescence from the 2.526 eV centre, which is associated with the slip planes in diamonds containing B nitrogen, provides evidence that changes are taking place at the slip planes. Emission from this centre can also originate from growth planes [13], and it is assumed that the residual 2.526-eV luminescence (typically 10–20% of the original) observed in some diamonds is associated with growth, rather than slip.

At the higher annealing temperature, in addition to the increase in the N3 and H3 absorption, single substitutional nitrogen is produced by the break-up of some A aggregates. The presence of this form of nitrogen favours some (N–V–N) centres being in the negative charge state, thereby producing absorption in the H2 band, and giving a green component to the colour. A small amount of $(N–V)^-$ absorption, and some 1344 cm^{-1} absorption may also be observed. By using a combination of temperature and pressure very close to the diamond–graphite stability line many of the diamonds become strongly luminescent. The specimens then share some of the characteristics of the rare natural diamonds described as 'green transmitters'.

Many phenomena that occur in diamond at geological temperatures (typically 750–1300°C [12]) over extremely long timescales (10^9 years, or more) can be simulated in the laboratory at much higher temperatures in much shorter periods. However, the end results are not always the same. In particular, we note that in natural diamonds the aggregation of single nitrogen goes virtually to completion, whereas the reverse reaction at higher temperatures precludes this being done in the laboratory.

We assume that the green transmitters encountered in nature are stones which had experienced plastic deformation followed by a long period of annealing. (It is probable that most plastically deformed diamonds experienced this deformation during eruption to the surface, and that a relatively modest amount of annealing occurred thereafter. These diamonds are therefore brown, rather than being green transmitters.) However, this natural annealing does not produce strong H2 absorption, and, in a diamond containing both A and B nitrogen there will certainly be no absorption at 1344 cm^{-1}. The green-luminescing diamonds that result from HPHT annealing at approximately 2025°C are therefore easily differentiated from the natural green transmitters.

In retrospect it is probable that the batch of green transmitters, with strong H2 absorption, examined recently by Buerki et al. [25] were originally brown diamonds that had been treated at HPHT by a process similar to that being used by NovaDiamond. (It is known, for example, that Russian groups are subjecting

natural brown diamonds to HPHT treatment, and supplying them to the gem market [26,27].) Buerki et al. made the reasonable assumption that the diamonds they examined had been irradiated and annealed at approximately 1400°C, since this procedure is known to produce H2 absorption [22]. However, one of the diamonds (labelled #334), for which they show spectra, has the majority of the nitrogen in the B form, but shows no H4 absorption. That situation would not be produced by radiation damage and annealing at 1400°C [23], but it is entirely typical of diamonds that have been annealed at 2025°C. Buerki et al. rightly believed that the diamonds they examined were artificially coloured, but almost certainly for the wrong reasons.

6. Postscript

After this paper was submitted, one of the authors (ATC) had the opportunity to examine two diamonds before and after they had been processed by NovaDiamond. One specimen, weighing 357 mg (1.79 carat), was brown, with the coloured graining characteristic of plastically deformed type Ia diamonds. The total nitrogen concentration was approximately 650 ppm, with approximately 80% present as B aggregates. After processing, this stone had a similar yellow/green colour to the specimens described in Section 3.2 and, like those specimens, exhibited green luminescence in white light.

The second diamond, weighing 372 mg (1.86 carat), was a pale yellow cape stone in which the colour was exclusively due to absorption in the N2 and N3 bands. There was no evidence in this diamond for plastic deformation. The specimen contained a total nitrogen concentration of approximately 1500 ppm with approximately equal quantities present as A and B aggregates. After processing, the diamond had an intense yellow colour, but did not exhibit any luminescence in white light.

The absorption spectra of this diamond before and after processing are shown in Fig. 6. The continuous absorption at high energies, present after processing (Fig. 6b), is caused by single substitutional nitrogen, at a concentration of approximately 25 ppm. It is just possible to detect absorption in the H3 and H2 (not shown) zero-phonon lines, but the absorption is negligible in comparison to that produced in the brown diamonds, and makes no significant contribution to the colour.

These observations substantially confirm the interpretations outlined in Section 4.3. Because the cape stone contained a negligible amount of plastic deformation, virtually no vacancies were released during the HPHT treatment and consequently only very small concentrations of H3 and H2 centres were produced. In the absence of H3 absorption, very clear evidence

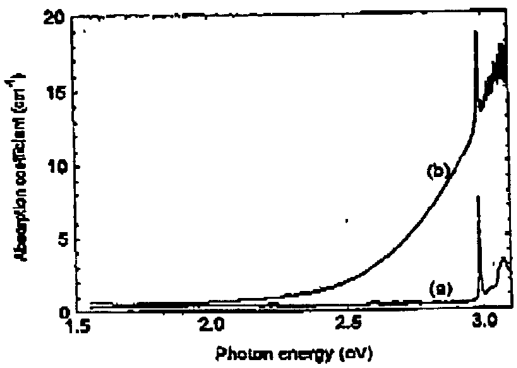

Fig. 6. Absorption spectra in the visible region of a cape stone (a) before, and (b) after, HPHT processing at approximately 2025°C. The spectra were measured with the diamond at 77 K.

can be seen for the production of single nitrogen atoms [from the break-up of A aggregates — see Eq. (1)], resulting in the continuous absorption in Fig. 6b. It was also possible, in this diamond, to detect the 1344-cm^{-1} absorption peak characteristic of single nitrogen atoms, although this was difficult because of the intensity of the pre-existing absorption in this region. In addition, this diamond and the brown diamond had a weak absorption at approximately 1480 cm^{-1} in the infrared spectrum, which was not present before processing. A peak at around this position has been reported previously [28] in diamonds subjected to HPHT treatment in the range 2500–2750°C.

Diamonds which exhibit absorption in the visible region characteristic of a type Ib diamond, but which have an infrared spectrum showing that the nitrogen is predominantly present as A and B aggregates, are encountered very rarely in nature. There is therefore a high probability that a diamond with such a spectrum has been processed at HPHT, and further tests would be required to determine whether the colour were natural.

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References

[1] E. Fritsch, In: G.E. Harlow (Ed.), The Nature of Diamonds, Cambridge University Press, UK, 1998, pp. 23–47.
[2] B. Woodburn, Rapaport Diamond Rep. 22 (36) (1999) 37.

[3] M.L. Johnson, J.I. Koivula, S.F. McClure, D. DeGhionno, Gems Gemol. 35 (2) (1999) 144.
[4] T.M. Moses, J.E. Shigley, S.F. McClure, J.I. Koivula, M. Van Daele, Gems Gemol. 35 (3) (1999) 14.
[5] T. Templeman, Rapaport Diamond Rep. 23 (1) (2000) 1.
[6] H. Kanda, M. Akaishi, N. Setaka, S. Yamaoka, O. Fukunaga, J. Mater. Sci. 15 (1980) 2743.
[7] A.R. Lang, Nature 213 (1967) 248.
[8] A.T. Collins, Diamond Relat. Mater. 8 (1999) 1455.
[9] R.M. Chrenko, R.E. Tuft, H.M. Strong, Nature 270 (1977) 141.
[10] M.R. Brozel, T. Evans, R.F. Stephenson, Proc. R. Soc London A 361 (1978) 109.
[11] T. Evans, Z. Qi, Proc. R. Soc. London A 381 (1982) 159.
[12] T. Evans, in: J.E. Field (Ed.), The Properties of Natural and Synthetic Diamond, Academic Press, London, 1992, pp. 259–290.
[13] A.T. Collins, G.S. Woods, Philos. Mag. B 45 (1982) 385.
[14] E.J. Brookes, A.T. Collins, G.S. Woods, J. Hard Mater. 4 (1993) 97.
[15] G. Davies, M.F. Hamer, Proc. R. Soc. London A 348 (1976) 285.
[16] G. Davies, J. Phys. C 5 (1972) 2534.
[17] M.D. Crossfield, G. Davies, A.T. Collins, E.C. Lightowlers, J. Phys. C: Solid State Phys. 7 (1974) 1909.
[18] A.T. Collins, Inst. Phys. Conf. Ser. 46 (1979) 327.
[19] A.T. Collins, J. Phys. C: Solid State Phys. 13 (1980) 2641.
[20] Y. Mita, Y. Nisida, K. Suito, A. Onodera, S. Yazu, J. Phys.: Condens. Matter 2 (1990) 8567.
[21] S.C. Lawson, G. Davies, A.T. Collins, A. Mainwood, J. Phys.: Condens. Matter 4 (1992) 3439.
[22] G.S. Woods, personal communication.
[23] G.S. Woods, A.T. Collins, J. Gemm. 20 (1986) 75.
[24] A.M. Zaitsev, in: M.A. Prelas, G. Popovici, K.E. Bigelow (Eds.), Handbook of Industrial Diamonds and Diamond Films, Marcel Dekker, New York, 1997, pp. 227–376.
[25] P.R. Buerki, I.M. Reinitz, S. Muhlmeister, S. Elen, Diamond Relat. Mater. 8 (1999) 1061.
[26] Jewellery News Asia, No. 169, September 1998, pp. 320, 322.
[27] U. Henn, C.C. Milisenda, Z. Dtsch. Gemmol. Ges. 48 (1999) 43.
[28] I. Kiflawi, J. Bruley, W. Luyten, G. van Tendeloo, Philos. Mag. B78 (1998) 299.